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(54) WEATHERABLE BLOCK COPOLYESTERCARBONATES AND BLENDS CONTAINING THEM

**WITTERUNGSBESTÄNDIGE BLOCKCOPOLYESTERCARBONATE UND DIESE ENTHALTENDE
POLYMERLEGIERUNGEN**

**COPOLYESTERCARBONATES SEQUENCES RESISTANT AUX INTEMPERIES ET MELANGES
LES RENFERMANT**

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Description

BACKGROUND OF THE INVENTION

5 [0001] This invention relates to resinous compositions of matter, and more specifically to block copolyestercarbonates having improved weatherability.

[0002] Polycarbonates and polyesters, especially poly(alkylene dicarboxylates), and blends thereof are widely employed classes of polymers, in part because of their excellent physical properties including high impact strength. However, their long term color instability is a problem. It causes yellowing, detracting from the transparency and attractiveness of the polymers. Loss of gloss can also be an undesirable long term phenomenon.

10 [0003] Yellowing of polycarbonates and polyesters is caused largely by the action of ultraviolet radiation, which is why such yellowing is frequently designated "photoyellowing". Numerous means for suppressing photoyellowing have been employed and proposed. Many of these involve incorporation in the polycarbonate of ultraviolet absorbing compounds (UVA's). For the most part, UVA's are low molecular weight compounds and they must be employed at relatively low levels, typically up to 1 % by weight, to avoid degradation of the physical properties of the polymer such as impact strength and high temperature properties as reflected in heat distortion temperature.

[0004] Other polymers have been blended with polycarbonates and/or polyesters to improve their resistance to degradation by ultraviolet radiation and loss of gloss, hereinafter sometimes collectively designated "weatherability". Examples of blends of this type are weatherable blends of polycarbonates with copolyesters comprising resorcinol iso/terephthalate units, optionally in combination with "soft block" ester units derived from an aliphatic or alicyclic dihydroxy compound or dicarboxylic acid. However, such blends are immiscible and their use is, therefore, limited to situations in which transparency is not required. In addition, it is of interest to produce a wider variety of weatherable and weatherability-improving polymers.

20 [0005] Japanese Kokai 56/133,332 describes copolyestercarbonates "having a highly alternating orientation". They are prepared by a 2-step process in which the first step is preparation of a hydroxy-terminated polyester oligomer having a degree of polymerization of 1-2 and the second step is treatment of said oligomer with a carbonyl halide such as phosgene to afford a final product having essentially alternating polyester and polycarbonate linkages; i.e., the degree of polymerization of the carbonate blocks is also about 1-2. These copolyestercarbonates are alleged to have excellent heat resistance, solvent resistance and moldability. No details of their weatherability are provided.

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SUMMARY OF THE INVENTION

[0006] The present invention is based on the discovery of a class of block copolyestercarbonates having excellent weatherability. Blends of said copolyestercarbonates with other polymers, specifically polycarbonates and polyesters, are resistant to loss of gloss and have excellent physical properties.

35 [0007] One aspect of the invention, therefore, is block copolyestercarbonates comprising organic carbonate blocks alternating with arylate blocks, said arylate blocks comprising arylate structural units derived from a 1,3-dihydroxybenzene and at least one aromatic dicarboxylic acid and having a degree of polymerization of at least 4.

[0008] Another aspect is block copolymers obtained by Fries rearrangement of a block copolyestercarbonate as described above.

40 [0009] Another aspect is compositions comprising resinous blends of block copolyestercarbonates as described above with at least one other polymer selected from the group consisting of polycarbonates, poly(alkylene dicarboxylates) and addition polymers, and any reaction products of said blends.

[0010] Still another aspect is a method for preparing block copolyestercarbonates which comprises:

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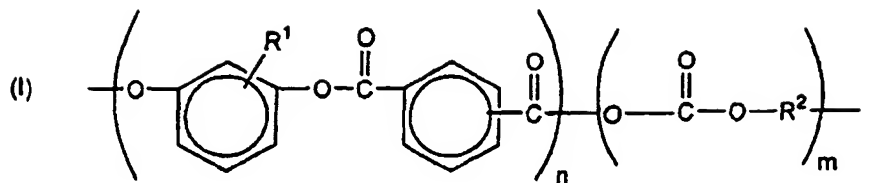
(A) preparing a hydroxy-terminated polyester intermediate having a degree of polymerization of at least 4 by the reaction of a 1,3-dihydroxybenzene with at least one aromatic dicarboxylic acid chloride under alkaline conditions, and

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(B) conducting a reaction of said polyester intermediate with at least one organic dihydroxy compound and a carbonyl halide.

DETAILED DESCRIPTION; PREFERRED EMBODIMENTS

55 [0011] The block copolyestercarbonates of the present invention comprise alternating carbonate and arylate blocks. They include polymers comprising moieties of the formula

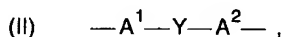


wherein R¹ is hydrogen, halogen or C₁₋₄ alkyl, each R² is independently a divalent organic radical, m is at least 10 and n is at least 4. The arylate blocks thus contain a 1,3-dihydroxybenzene moiety which may be substituted with halogen, usually chlorine or bromine, or with C₁₋₄ alkyl; i.e., methyl, ethyl, propyl or butyl. Said alkyl groups are preferably primary or secondary groups, with methyl being more preferred, and are most often located in the ortho position to both oxygen atoms although other locations are also contemplated. The most preferred moieties are resorcinol moieties, in which R¹ is hydrogen.

[0012] Said 1,3-dihydroxybenzene moieties are bound to aromatic dicarboxylic acid moieties which may be monocyclic moieties, e.g., isophthalate or terephthalate, or polycyclic moieties, e.g., naphthalenedicarboxylate. Preferably, the aromatic dicarboxylic acid moieties are isophthalate and/or terephthalate. Either or both of said moieties may be present. For the most part, both are present in a molar ratio of isophthalate to terephthalate in the range of 0.25-4.0:1, preferably 0.8-2.5:1.

[0013] In the carbonate blocks, each R² is independently an organic radical. For the most part, at least about 60 percent of the total number of R² groups in the polymer are aromatic organic radicals and the balance thereof are aliphatic, alicyclic, or aromatic radicals. Suitable R² radicals include m-phenylene, p-phenylene, 4,4'-biphenylene, 4,4'-bi(3,5-dimethyl)-phenylene, 2,2-bis(4-phenylene)propane and similar radicals such as those which correspond to the dihydroxy-substituted aromatic hydrocarbons disclosed by name or formula (generic or specific) in U.S. Patent 4,217,438.

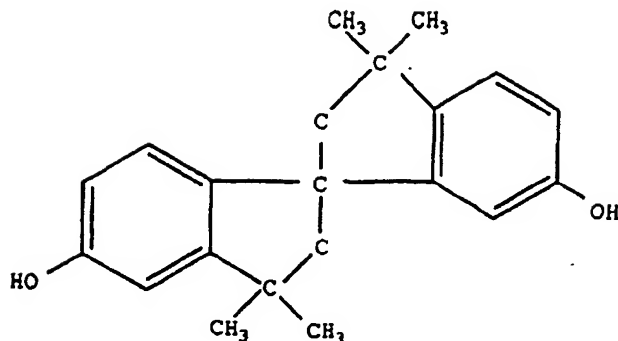
[0014] More preferably, each R² is an aromatic organic radical and still more preferably a radical of the formula



wherein each A¹ and A² is a monocyclic divalent aryl radical and Y is a bridging radical in which one or two carbon atoms separate A¹ and A². The free valence bonds in formula II are usually in the meta or para positions of A¹ and A² in relation to Y. Compounds in which R² has formula II are bisphenols, and for the sake of brevity the term "bisphenol" is sometimes used herein to designate the dihydroxy-substituted aromatic hydrocarbons; it should be understood, however, that non bisphenol compounds of this type may also be employed as appropriate.

[0015] In formula II, A¹ and A² typically represent unsubstituted phenylene or substituted derivatives thereof, illustrative substituents (one or more) being alkyl, alkenyl, and halogen (particularly bromine). Unsubstituted phenylene radicals are preferred. Both A¹ and A² are preferably p-phenylene, although both may be o- or m-phenylene or one o- or m-phenylene and the other p-phenylene.

[0016] The bridging radical, Y, is one in which one or two atoms, separate A¹ from A². The preferred embodiment is one in which one atom separates A¹ from A². Illustrative radicals of this type are -O-, -S-, -SO- or -SO₂-, methylene, cyclohexyl-methylene, 2-[2.2.1]-bicycloheptyl methylene, ethylene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecylidene, cyclododecylidene, adamantylidene, and the 2,2,2',2'-tetrahydro-3,3,3',3'-tetramethyl-1,1'spiro-bis[1H-indene]6,6'-diols having the following formula ;



Gem-alkylene (alkylidene) radicals are preferred. Also included, however, are unsaturated radicals. For reasons of availability and particular suitability for the purposes of this invention, the preferred bisphenol is 2,2-bis(4-hydroxyphenyl)propane ("BPA"), in which Y is isopropylidene and A¹ and A² are each p-phenylene.

[0017] The arylate blocks have a degree of polymerization (DP), represented by n, of at least 4, preferably at least 10, more preferably at least 20 and most preferably 30-150. The DP of the carbonate blocks, represented by m, is generally at least 10, preferably at least 20 and most preferably 50-200.

[0018] The distribution of the blocks may be such as to provide a copolymer having any desired weight proportion of arylate blocks in relation to carbonate blocks. In general, copolymers containing 10-90% by weight arylate blocks are preferred.

[0019] In step A of the method of this invention for the preparation of block copolyestercarbonates, a 1,3-dihydroxybenzene which may be resorcinol (preferably) or an alkyl- or haloresorcinol may be contacted under aqueous alkaline reactive conditions with at least one aromatic dicarboxylic acid chloride, preferably isophthaloyl chloride, terephthaloyl chloride or a mixture thereof. The alkaline conditions are typically provided by introduction of an alkali metal hydroxide, usually sodium hydroxide. A catalyst, most often a tetraalkylammonium, tetraalkylphosphonium or hexaalkylguanidinium halide, is usually also present, as is an organic solvent, generally a water-immiscible solvent and preferably a chlorinated aliphatic compound such as methylene chloride. Thus, the reaction is generally conducted in a 2-phase system.

[0020] In order to afford a hydroxy-terminated polyester intermediate, the molar ratio of resorcinol to acyl chlorides is preferably greater than 1:1; e.g., in the range of 1.01-1.90:1. Base may be present in a molar ratio to acyl halides of 2-2.5:1. Catalyst is usually employed in the amount of 0.1-10 mole percent based on combined acyl halides. Reaction temperatures are most often in the range of 25-50°C.

[0021] Following the completion of polyester intermediate preparation, it is sometimes advantageous to acidify the aqueous phase of the two-phase system with a weak acid prior to phase separation. The organic phase, which contains the polyester intermediate, is then subjected to step B which is the block copolyestercarbonate-forming reaction. It is also contemplated, however, to proceed to step B without acidification or separation, and this is often possible without loss of yield or purity.

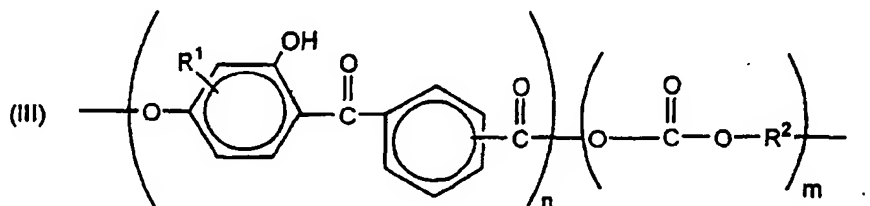
[0022] It is also within the scope of the invention to prepare the polyester intermediate entirely in an organic liquid, with the use of a base soluble in said liquid. Suitable bases for such use include tertiary amines such as triethylamine.

[0023] The dihydroxyaromatic compound employed in the second step typically has the formula HO-R²-OH, wherein R² is as previously defined. Bisphenol A is generally preferred. The carbonyl halide is preferably phosgene. This reaction may be conducted according to art-recognized interfacial procedures (i.e., also in a 2-phase system), employing a suitable interfacial polymerization catalyst and an alkaline reagent, again preferably sodium hydroxide, and optionally a branching agent such as 1,1,1-tris(4-hydroxyphenyl)ethane and/or a chain termination agent such as phenol or p-cumylphenol. To suppress scrambling of the block copolymer, the pH is maintained at a relatively low level, typically in the range of about 5-9, for the initial part of the phosgenation reaction; it may be increased to about 10-13 during the latter part of said reaction.

[0024] Following completion of both reactions, the block copolyestercarbonate may be isolated by conventional procedures. These may include, for example, anti-solvent precipitation, drying and pelletization via extrusion. It is also contemplated to conduct the first step by other ester-forming methods, as illustrated by transesterification using aromatic diesters and a 1,3-dihydroxybenzene either in a solvent or in the melt.

[0025] The block copolyestercarbonates of this invention are polymers having excellent physical properties. Their light transmitting properties are similar to those of polycarbonates. Thus, they are substantially transparent and may be employed as substitutes for polycarbonates in the fabrication of transparent sheet material when improved weatherability is mandated.

[0026] It is believed that the weatherability and other beneficial properties of the block copolyestercarbonates of the invention is attributable, at least in part, to the occurrence of a thermally or photochemically induced Fries rearrangement of the arylate blocks therein, to yield benzophenone moieties which serve as light stabilizers. For example, the moieties of formula I can rearrange to yield moieties of the formula



wherein R^1 , R^2 , m and n are as previously defined. It is also contemplated to introduce moieties of formula III via synthesis and polymerization.

[0027] The block copolyestercarbonates may also be employed as weatherability-improving additives for other polymers, especially polycarbonates, polyesters and addition polymers. The polycarbonates in the blend compositions of the invention are, for the most part, similar in molecular structure to the carbonate blocks of the block copolyestercarbonate as described hereinabove, with bisphenol A homo- and copolycarbonates generally being preferred. The polyesters are most often poly(alkylene dicarboxylates) and especially poly(alkylene arenedioates), with poly(ethylene terephthalate) and poly(1,4-butylene terephthalate) being preferred. Addition polymers include homopolymers and copolymers, especially copolymers of alkenylaromatic compounds, such as styrene, with ethylenically unsaturated nitriles, such as acrylonitrile and methacrylonitrile; dienes, such as butadiene and isoprene; and acrylic monomers, such as ethyl acrylate. These include the ABS (acrylonitrile-butadiene-styrene) and ASA (acrylonitrile-styrene-alkyl acrylate) graft copolymers.

[0028] The blend compositions of the invention may be prepared by such conventional operations as solvent blending and melt blending as by extrusion. They may additionally contain art-recognized additives including pigments, dyes, impact modifiers, stabilizers, flow aids and mold release agents. It is intended that the blend compositions include simple physical blends and any reaction products thereof, as illustrated by polyester-polycarbonate transesterification products.

[0029] Proportions of the block copolyestercarbonates in such blends are determined chiefly by the resulting proportions of arylate blocks, which are the active weatherability-improving entities, typical proportions providing about 10-50% by weight of arylate blocks in the blend. By reason of some degree of incompatibility between the block copolyestercarbonates of the invention and the polycarbonates and polyesters in which they may be incorporated, said blends are often not transparent. However, transparent blends may be prepared by adjusting the length of the arylate blocks in the block copolyestercarbonates. The other properties of said blends are excellent.

[0030] The block copolyestercarbonates of the invention, and blends thereof, may be used in various applications, especially those involving outdoor use and storage and hence requiring resistance to weathering. These include automotive body panels and trim; outdoor vehicles and devices such as lawn mowers, garden tractors and outdoor tools; lighting appliances; and enclosures for electrical and telecommunications systems.

[0031] The invention is illustrated by the following examples. All percentages and ratios are by weight unless otherwise indicated. Molecular weights were determined in chloroform by gel permeation chromatography relative to polystyrene and are reported as weight average (M_w) or number average (M_n).

EXAMPLES 1-10

[0032] A number of 1-l 4-necked flasks fitted with mechanical stirrers, nitrogen inlets, reflux condensers and two pressure-equalized addition funnels were charged with 5 mmol of tetra-n-butylammonium bromide (TBAB) or methyltri-n-butylammonium chloride (MTBAC), various amounts of resorcinol and 150 ml of degassed methylene chloride. The flasks were then purged with nitrogen and the addition funnels were charged with 212 mmol of 15% aqueous sodium hydroxide solution, maintained at 20°C and purged with nitrogen, and various degassed mixtures of isophthaloyl chloride and terephthaloyl chloride dissolved in 100 ml of methylene chloride.

[0033] The sodium hydroxide solutions were added to the flasks under nitrogen, with stirring, whereupon the resorcinol dissolved to form translucent 2-phase mixtures. The isophthaloyl/terephthaloyl chloride mixtures were then added, with continued stirring, whereupon exotherms caused weak reflux. Stirring was continued for one hour at 35°C. The mixtures were then acidified with phosphorous acid to a pH of 3, the two phases were separated and the molecular

weights of the resulting polyester intermediates were determined.

[0034] The polyester intermediate solutions were charged to phosgenation reactors fitted with stirrers, reflux condensers, phosgene inlets and pH-controlled sodium hydroxide delivery systems. There were added various proportions of bisphenol A, 2 mole percent (based on bisphenol A) of p-cumylphenol and, for each 100 mmol of bisphenol A, 0.1 ml of triethylamine and 0.5 ml of water. Phosgene, 120 mmol per 100 mmol of bisphenol A, was passed into the mixtures over 22 minutes, with pH control by addition of 30% aqueous sodium hydroxide solution, in the range of 8-9 until the final 5 minutes whereupon the pH was raised to 10.5-11.

[0035] The mixtures were acidified with dilute hydrochloric acid solution and the organic phases were separated and washed with water. The desired block copolyestercarbonates were precipitated by pouring into methanol and dried overnight at 60°C.

[0036] The results of the various examples are given in Table I. Examples 6-9 represent larger scale reactions (2.2 kg per batch).

TABLE I

Ex.	Catalyst	Molar ratio, isophthaloyl/ terephthaloyl	Polyester intermediate, M_w	Polyester intermediate', M_n	Resorcinol, mole % excess	Product, % polyester blocks	Product M_w
1	TBAB	50/50	19,200	9,500	5	35	73,000
2	TBAB	50/50	16,900	8,300	5	35	95,000
3	MTBAC	50/50	17,000	8,600	5	50	99,000
4	TBAB	50/50	12,500	6,200	10	50	75,200
5	TBAB	70/30	32,300	16,100	3	50	86,500
6	MTBAC	50/50	17,200	8,900	5	50	90,700
7	MTBAC	50/50	32,400	16,500	3	50	81,200
8	MTBAC	50/50	14,500	7,200	5	80	78,100
9	MTBAC	50/50	24,300	12,100	5	20	75,100
10	MTBAC	50/50	53,500	28,100	3	20	67,300

EXAMPLE 11

[0037] Samples (2 g) of the product of Example 6 and several other materials, described hereinafter, were dissolved in methylene chloride or chloroform (8 ml) and films with a thickness of about 250 microns were drawn on glass plates with a doctor blade. The solvents were evaporated, leaving films approximately 40 microns thick which were floated from the glass plates with water. The haze values of the films were determined using a Gardner XL-835 haze meter.

[0038] The results are given in Table II. The following other materials were evaluated: a commercial bisphenol A polycarbonate (PC), a resorcinol polyarylate having a ratio of isophthalate to terephthalate groups of 1:1 and a molecular

weight of about 50,000 (RPA), a blend of PC with the product of Example 6 and two PC-RPA blends.

TABLE II

Film material	Haze, %
Example 6	0.8
PC	0.8
RPA	0.8
PC/Ex. 6, 1.5:1	12.7
PC/RPA, 4:1	69.0
PC/RPA, 1:1	38.5

[0039] These results show the improved compatibility of blends of the block copolyestercarbonate of Example 6 with polycarbonate, as compared with polyarylates not containing carbonate blocks.

EXAMPLES 12-16

[0040] To 1-l 3-necked flasks equipped with reflux condensers, mechanical stirrers and pressure equilibration addition funnels were added various amounts of resorcinol and triethylamine and 100 ml of methylene chloride. The flasks were blanketed with nitrogen and solutions of 10.151 g (50 mmol) each of isophthaloyl chloride and terephthaloyl chloride in 150 ml of methylene chloride were added dropwise over 4-8 minutes, so as to maintain a gentle reflux. The mixtures were further stirred at reflux temperature for 30 minutes, then transferred to separation funnels and washed once with water, twice with dilute aqueous hydrochloric acid and again with water.

[0041] The oligomer solutions were transferred to phosgenation reactors similar to those of Examples 1-10. After addition of bisphenol A, triethylamine (1 mole percent based on bisphenol A), water and p-cumylphenol as a chain termination agent, the phosgenation was conducted as described in said examples.

[0042] The results and product parameters are given in Table III. All of the copolymers contained 50% polyarylate units.

TABLE III

Ex.	Resorcinol, g	Triethylamine, ml	Bisphenol A, g	CH ₂ Cl ₂ for phosgenation, ml	Water for phosgenation, ml	Polyester intermediate, Mw	Polyester intermediate, Mn	Product Mw
12	13.76	36	22	250	50	10,500	3,500	77,200
13	12.23	32	21.7	250	50	20,000	6,300	85,500
14	11.59	32	21.5	250	50	28,500	10,700	86,300
15	11.236	31	21.2	250	50	43,700	13,500	90,500
16	22.02	58	31	300	55	3,550	1,440	32,700

EXAMPLE 17

[0043] Various block copolyestercarbonates of Examples 12-16 were solution blended with a commercially available bisphenol A polycarbonate, and films were cast from these solutions using the procedure of Example 11. Haze measurements were made and are given in Table IV.

TABLE IV

Copolymer ex.	Copolymer, g	PC, g	Haze, %
12	0.4	1.6	4.32
12	0.8	1.2	5.54
12	1.0	1.0	22.6
12	1.5	0.5	14.6
12	2.0	0.0	0.33
13	2.0	0.0	0.27
14	2.0	0.0	0.29
15	2.0	0.0	0.22
16	0.4	1.6	0.58
16	0.8	1.2	1.09
16	1.0	1.0	1.27
16	1.5	0.5	2.75
16	2.0	0.0	0.39

[0044] It is apparent that the neat copolymers, as well as some of the blends using the copolyestercarbonate of Example 16, gave essentially transparent, haze-free films.

EXAMPLE 18

[0045] Blends of PC with various proportions of RPA or of the product of Example 6 and with various colorants (titanium dioxide at 2%, carbon black at 0.6%, black dye at 0.47%) were prepared by dry blending followed by extrusion and were injection molded into test samples. The samples were subjected to accelerated weathering tests in an Atlas Ci35a xenon arc weatherometer equipped with borosilicate inner and outer filters at an irradiance of 0.77 W/m² at 340 nm, using cycles of 160 min light, 5 min dark and 15 min dark with water spray. The proportions of gloss retention (60° angle) after a total exposure of 935 kJ/m² are listed in Table V.

TABLE V

Polymers	Colorant	Gloss retention, %
PC	Titanium dioxide	17
PC/RPA 10%	Titanium dioxide	14
PC/RPA 20%	Titanium dioxide	30
PC/Ex. 6 10%	Titanium dioxide	36
PC/Ex. 6 20%	Titanium dioxide	37
PC	Carbon black	11
PC/RPA 10%	Carbon black	22
PC/RPA 20%	Carbon black	58
PC/Ex. 6 10%	Carbon black	40
PC/Ex. 6 20%	Carbon black	69

TABLE V (continued)

Polymers	Colorant	Gloss retention, %
PC	Black dye	70
PC/RPA 10%	Black dye	55
PC/RPA 20%	Black dye	77
PC/Ex. 6 10%	Black dye	70
PC/Ex. 6 20%	Black dye	87

[0046] These results show the improvement in weatherability afforded by the block copolyestercarbonates of the invention in comparison with a simple polyarylate and with neat polycarbonate.

EXAMPLE 19

[0047] Blends of PC, 30% of a commercially available poly(1,4-butylene terephthalate) (PBT) and 0.47% of the black dyes of Example 18 were dry blended, extruded and injection molded into test specimens which were evaluated in the apparatus of Example 18, alone and in combination with RPA and the product of Example 6. The light exposure required, in kJ/m² of energy at 340 nm, to cause 50% loss of gloss was determined for each specimen and the results are given in Table VI.

TABLE VI

PC, %			Exposure,
	RPA, %	Ex. 6, %	kJ/m ²
70	--	--	420
50	20	--	864
30	--	40	1,400

[0048] It is again apparent that the presence of the block copolyestercarbonate of the invention improves the weatherability of the blend to a significant extent.

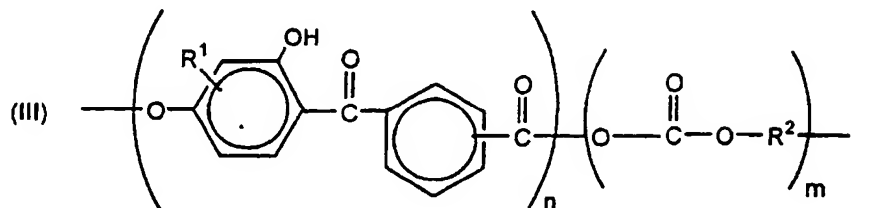
Claims

1. A block copolyestercarbonate comprising organic carbonate blocks alternating with arylate blocks, said arylate blocks comprising arylate structural units derived from a 1,3-dihydroxybenzene and at least one aromatic dicarboxylic acid and having a degree of polymerization of at least 4.
2. A block copolyestercarbonate according to claim 1 wherein the carbonate blocks consist of bisphenol A carbonate units.
3. A block copolyestercarbonate according to claim 1 wherein the degree of polymerization of the carbonate blocks is at least 10.
4. A block copolyestercarbonate according to claim 1 wherein the arylate blocks are resorcinol isophthalate or resorcinol terephthalate blocks or a mixture thereof.
5. A block copolyestercarbonate according to claim 4 wherein the arylate blocks are derived from a mixture of isophthalic and terephthalic acids.
6. A block copolyestercarbonate according to claim 5 wherein the molar ratio of isophthalate to terephthalate in the arylate blocks is in the range of 0.25-4.0:1.
7. A block copolyestercarbonate according to claim 5 wherein the degree of polymerization of the arylate blocks is

at least 10.

8. A block copolyestercarbonate according to claim 5 which consists of 10-90% by weight arylate blocks.

9. A block copolyestercarbonate comprising moieties of the formula

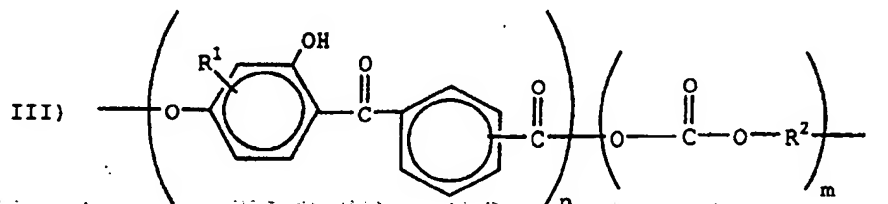


wherein R^1 is hydrogen, halogen or C_{1-4} alkyl, each R^2 is independently a divalent organic radical, m is at least 10 and n is at least 4.

10. A block copolyestercarbonate according to claim 9 wherein R^1 is hydrogen, R^2 is p-phenyleneisopropylidene, n is at least 10 and m is at least 20, said copolyestercarbonate consisting of isophthalate and terephthalate ester blocks in a molar ratio in the range of 0.8-2.5:1.

11. A block copolymer obtained by Fries rearrangement of a block copolyestercarbonate according to claim 1.

12. A block copolymer according to claim 11 comprising moieties of the formula



wherein R^1 is hydrogen, halogen or C_{1-4} alkyl, each R^2 is independently a divalent organic radical, m is at least 10 and n is at least 5.

13. A block copolymer according to claim 12 wherein R^1 is hydrogen, R^2 is p-phenyleneisopropylidene, n is at least 10 and m is at least 20, said copolyestercarbonate consisting of isophthalate and terephthalate ester blocks in a molar ratio in the range of 0.8-2.5:1.

14. A composition comprising a resinous blend of a block copolyestercarbonate according to claim 1 with at least one other polymer selected from the group consisting of polycarbonates, poly(alkylene dicarboxylates) and addition polymers, and any reaction products thereof.

15. A blend according to claim 14 wherein the other polymer is a polycarbonate.

16. A blend according to claim 15 wherein the other polymer is a bisphenol A polycarbonate.

17. A blend according to claim 14 wherein the other polymer is a poly(alkylene dicarboxylate).

18. A blend according to claim 17 wherein the other polymer is poly(1,4-butylene terephthalate).

19. A blend according to claim 17 wherein the other polymer is poly(ethylene terephthalate).

20. An article made from the composition of claim 14.

21. An article according to claim 20 comprising an enclosure for an electrical and telecommunications system.

5 22. A method for preparing a block copolyestercarbonate which comprises:

(A) preparing a hydroxy-terminated polyester intermediate having a degree of polymerization of at least 4 by the reaction of a 1,3-dihydroxybenzene with at least one aromatic dicarboxylic acid chloride under alkaline conditions, and

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(B) conducting a reaction of said polyester intermediate with at least one organic dihydroxy compound and a carbonyl halide.

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23. A method according to claim 22 wherein the molar ratio of resorcinol or alkylresorcinol to acyl chlorides in step A is in the range of 1.01-1.90:1.

24. A method according to claim 22 wherein the 1,3-dihydroxybenzene in step A is resorcinol and the dicarboxylic acid chloride is isophthaloyl chloride, terephthaloyl chloride or a mixture thereof.

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25. A method according to claim 22 wherein the organic dihydroxy compound in step B is bisphenol A and the carbonyl halide is phosgene.

26. A method according to claim 22 wherein steps A and B are both conducted in a 2-phase system including an aqueous phase and a water-immiscible organic solvent.

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27. A method according to claim 22 wherein the pH in step B is maintained in the range of 5-9 for the initial part and increased to 10-13 during the latter part of said reaction.

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28. A block copolyester carbonate according to claim 1, wherein the arylate blocks have a degree of polymerization of at least 10.

29. A block copolyester carbonate according to claim 1, wherein the arylate blocks have a degree of polymerization of at least 20.

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30. A block copolyester carbonate according to claim 1, wherein the arylate blocks have a degree of polymerization of 30-150.

31. A block copolyester carbonate according to claim 1, wherein the carbonate blocks have a degree of polymerization of at least 20.

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32. A block copolyester carbonate according to claim 1 wherein the carbonate blocks have a degree of polymerization of 50-200.

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Patentansprüche

1. Blockcopolyestercarbonat, das organische Carbonatblöcke umfasst, die mit Arylatblöcken alternieren, wobei die Arylatblöcke Arylatstruktureinheiten umfassen, welche aus einem 1,3-Dihydroxybenzol und mindestens einer aromatischen Dicarbonsäure abgeleitet sind, und einen Polymerisationsgrad von mindestens 4 besitzen.

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2. Blockcopolyestercarbonat nach Anspruch 1, worin die Carbonatblöcke aus Bisphenol-A-Carbonateinheiten bestehen.

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3. Blockcopolyestercarbonat nach Anspruch 1, worin der Polymerisationsgrad der Carbonatblöcke mindestens 10 beträgt.

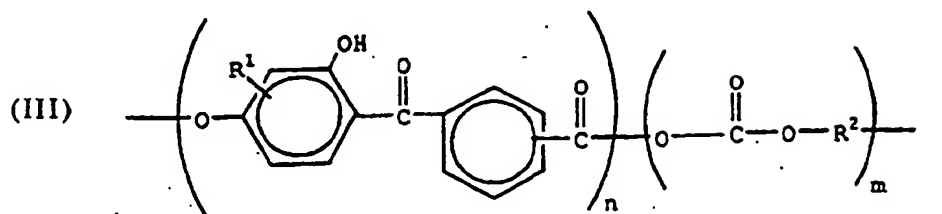
4. Blockcopolyestercarbonat nach Anspruch 1, worin die Arylatblöcke Resorcinol-Isophthalat oder Resorcinol-Terephthalatblöcke oder eine Mischung davon sind.
5. Blockcopolyestercarbonat nach Anspruch 4, worin die Arylatblöcke aus einer Mischung von Isophthal- und Terephthalsäuren abgeleitet sind.
6. Blockcopolyestercarbonat nach Anspruch 5, worin das Molverhältnis von Isophthalat zu Terephthalat in den Arylatblöcken im Bereich von 0,25-4,0:1 liegt.
7. Blockcopolyestercarbonat nach Anspruch 5, worin der Polymerisationsgrad der Arylatblöcke mindestens 10 beträgt.
8. Blockcopolyestercarbonat nach Anspruch 5, das zu 10-90 Gew.-% aus Arylatblöcken besteht.
9. Blockcopolyestercarbonat, das Komponenten der Formel umfasst, worin R¹ ein Wasserstoff, ein Halogen oder eine C₁₋₄ Alkylgruppe ist, jeder R² unabhängig voneinander ein divalenter organischer Rest ist, m mindestens 10 beträgt und n mindestens 4 beträgt.
10. Blockcopolyestercarbonat nach Anspruch 9, worin R¹ Wasserstoff ist, R² p-Phenylenisopropyliden ist, n mindestens 10 beträgt und m mindestens 20 beträgt, wobei das Copolyestercarbonat aus Isophthalat- und Terephthalatesterblöcken in einem Molverhältnis im Bereich von 0,8-2,5:1 besteht.
11. Blockcopolymer, das durch Friessche Umlagerung eines Blockcopolyestercarbonats nach Anspruch 1 erhalten ist.
12. Blockcopolymer nach Anspruch 11, das Komponenten der Formel umfasst, worin R¹ ein Wasserstoff, ein Halogen oder eine C₁₋₄ Alkylgruppe ist, jeder R² unabhängig voneinander ein divalenter organischer Rest ist, m mindestens 10 beträgt und n mindestens 5 beträgt.
13. Blockcopolymer nach Anspruch 12, worin R¹ Wasserstoff ist, R² p-Phenylenisopropyliden ist, n mindestens 10 beträgt und m mindestens 20 beträgt, wobei das Copolyestercarbonat aus Isophthalat- und Terephthalatesterblöcken in einem Molverhältnis im Bereich von 0,8-2,5:1 besteht.
14. Zusammensetzung, umfassend eine harzartige Mischung von einem Blockcopolyestercarbonat nach Anspruch 1 mit mindestens einem anderen Polymer, das aus der Gruppe der Polycarbonate, Poly(alkylendicarboxylate) und Additionspolymere und jeglicher Reaktionsprodukte davon ausgewählt ist.
15. Mischung nach Anspruch 14, worin das andere Polymer ein Polycarbonat ist.
16. Mischung nach Anspruch 15, worin das andere Polymer ein Bisphenol-A-Polycarbonat ist.
17. Mischung nach Anspruch 14, worin das andere Polymer ein Poly(alkylendicarboxylat) ist.
18. Mischung nach Anspruch 17, worin das andere Polymer Poly(1,4-butylenterephthalat) ist.
19. Mischung nach Anspruch 17, worin das andere Polymer Poly(ethylenterephthalat) ist.
20. Artikel, der aus der Zusammensetzung nach Anspruch 14 hergestellt ist.
21. Artikel nach Anspruch 20, der ein Gehäuse für eine elektrische und Telekommunikationsanlage umfasst.
22. Verfahren zur Herstellung eines Blockcopolyestercarbonats, bei dem man:
 - (A) durch die Reaktion eines 1,3-Dihydroxybenzols mit mindestens einem aromatischen Dicarbonsäurechlorid unter alkalischen Bedingungen ein hydroxyterminiertes Polyesterintermediat mit einem Polymerisationsgrad von mindestens 4 herstellt, und
 - (B) eine Reaktion des Polyesterintermediats mit mindestens einer organischen Dihydroxyverbindung und einem Carbonylhalogenid durchführt.

23. Verfahren nach Anspruch 22, worin das Molverhältnis von Resorcinol oder Alkylresorcinol zu den Acylchloriden in Schritt A im Bereich von 1,01-1,90:1 liegt.
24. Verfahren nach Anspruch 22, worin das 1,3-Dihydroxybenzol in Schritt A Resorcinol ist und das Dicarbonsäurechlorid Isophthaloylchlorid, Terephthaloylchlorid oder eine Mischung davon ist.
25. Verfahren nach Anspruch 22, worin die organische Dihydroxyverbindung in Schritt B Bisphenol-A ist und das Carbonylhalogenid Phosgen ist.
26. Verfahren nach Anspruch 22, worin die Schritte A und B beide in einem Zweiphasensystem durchgeführt werden, das eine wässrige Phase und ein mit Wasser nicht mischbares organisches Lösungsmittel beinhaltet.
27. Verfahren nach Anspruch 22, worin der pH in Schritt B im Anfangsteil im Bereich von 5-9 beibehalten wird und während des späteren Teils der Reaktion auf 10-13 erhöht wird.
28. Blockcopolyestercarbonat nach Anspruch 1, worin die Arylatblöcke einen Polymerisationsgrad von mindestens 10 besitzen.
29. Blockcopolyestercarbonat nach Anspruch 1, worin die Arylatblöcke einen Polymerisationsgrad von mindestens 20 besitzen.
30. Blockcopolyestercarbonat nach Anspruch 1, worin die Arylatblöcke einen Polymerisationsgrad von 30-150 besitzen.
31. Blockcopolyestercarbonat nach Anspruch 1, worin die Carbonatblöcke einen Polymerisationsgrad von mindestens 20 besitzen.
32. Blockcopolyestercarbonat nach Anspruch 1, worin die Carbonatblöcke einen Polymerisationsgrad von 50-200 besitzen.

Revendications

1. Copolyestercarbonate séquencé, comprenant des séquences de carbonate organique alternant avec des séquences d'arylate, lesquelles séquences d'arylate comportent des motifs structuraux de type arylate, dérivés d'un 1,3-dihydroxybenzène et d'au moins un acide dicarboxylique aromatique, et présentent un degré de polymérisation d'au moins 4.
2. Copolyestercarbonate séquencé conforme à la revendication 1, dans lequel les séquences de carbonate sont constituées de motifs de carbonate de bisphénol A.
3. Copolyestercarbonate séquencé conforme à la revendication 1, dans lequel le degré de polymérisation des séquences de carbonate vaut au moins 10.
4. Copolyestercarbonate séquencé conforme à la revendication 1, dans lequel les séquences d'arylate sont des séquences d'isophthalate de résorcinol, de téréphthalate de résorcinol, ou d'un mélange de ces motifs.
5. Copolyestercarbonate séquencé conforme à la revendication 4, dans lequel les séquences d'arylate dérivent d'un mélange des acides isophthalique et téréphthalique.
6. Copolyestercarbonate séquencé conforme à la revendication 5, dans lequel, dans les séquences d'arylate, le rapport molaire de l'isophthalate au téréphthalate vaut de 0,25/1 à 4,0/1.
7. Copolyestercarbonate séquencé conforme à la revendication 5, dans lequel le degré de polymérisation des séquences d'arylate vaut au moins 10.
8. Copolyestercarbonate séquencé conforme à la revendication 5, qui est constitué, pour 10 à 90 % en poids, de séquences d'arylate.

9. Copolyestercarbonate séquencé comportant des motifs de formule

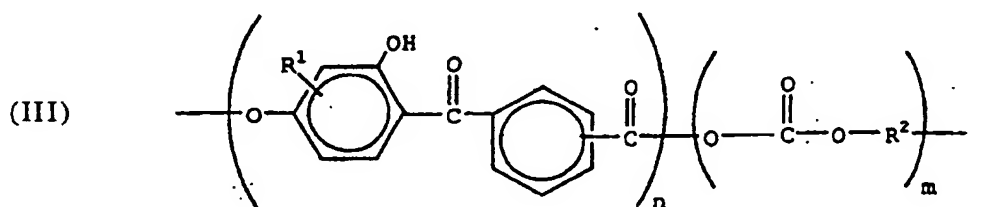


dans laquelle R' représente un atome d'hydrogène ou d'halogène ou un groupe alkyle en C₁₋₄, chaque R² représente indépendamment un groupe organique divalent, m vaut au moins 10 et n vaut au moins 4.

10. Copolyestercarbonate séquencé conforme à la revendication 9, dans lequel R¹ représente un atome d'hydrogène, R² représente un groupe p-phénylène-isopropylidène, n vaut au moins 10 et m vaut au moins 20, lequel copolyestercarbonate comporte des séquences d'esters isophtalate et téréphtalate en un rapport molaire de 0,8/1 à 2,5/1.

11. Copolymère séquencé obtenu par réarrangement de Fries d'un copolyestercarbonate séquencé conforme à la revendication 1.

12. Copolymère séquencé conforme à la revendication 11, comportant des motifs de formule



dans laquelle R¹ représente un atome d'hydrogène ou d'halogène ou un groupe alkyle en C₁₋₄, chaque R² représente indépendamment un groupe organique divalent, m vaut au moins 10 et n vaut au moins 5.

13. Copolymère séquencé conforme à la revendication 12, dans lequel R¹ représente un atome d'hydrogène, R² représente un groupe p-phénylène-isopropylidène, n vaut au moins 10 et m vaut au moins 20, ledit copolyestercarbonate comportant des séquences d'esters isophtalate et téréphtalate en un rapport molaire de 0,8/1 à 2,5/1.

14. Composition comprenant un mélange résineux d'un copolyestercarbonate conforme à la revendication 1 et d'au moins un autre polymère choisi dans l'ensemble constitué par les polycarbonates, les poly(dicarboxylates d'alkylène) et les polymères d'addition, ainsi que tous les produits de réaction de ces polymères.

15. Mélange conforme à la revendication 14, dans lequel l'autre polymère est un polycarbonate.

16. Mélange conforme à la revendication 15, dans lequel l'autre polymère est du polycarbonate de bisphénol A.

17. Mélange conforme à la revendication 14, dans lequel l'autre polymère est un poly(dicarboxylate d'alkylène):

18. Mélange conforme à la revendication 17, dans lequel l'autre polymère est du poly(téréphtalate de 1,4-butylène).

19. Mélange conforme à la revendication 17, dans lequel l'autre polymère est du poly(téréphtalate d'éthylène).

20. Article fait d'une composition conforme à la revendication 14

21. Article conforme à la revendication 20, comprenant une enveloppe pour systèmes électriques ou de télécommunications.

22. Procédé de préparation d'un copolyestercarbonate séquencé, qui comporte :

A) le fait de préparer un intermédiaire polyester à terminaisons hydroxy dont le degré de polymérisation vaut au moins 4, en faisant réagir un 1,3-dihydroxybenzène avec au moins un chlorure d'acide dicarboxylique aromatique, en milieu alcalin ;

B) et le fait de faire réagir ledit intermédiaire polyester avec au moins un composé organique dihydroxylé et un halogénure de carbonyle.

23. Procédé conforme à la revendication 22, dans lequel, dans l'étape (A), le rapport molaire du résorcinol ou de l'alkyl-résorcinol aux chlorures d'acyle vaut de 1,01/1 à 1,90/1.

24. Procédé conforme à la revendication 22, dans lequel, dans l'étape (A), le 1,3-dihydroxybenzène est du résorcinol et le chlorure d'acide dicarboxylique est du chlorure d'isophthaloyle, du chlorure de téréphthaloyle ou un mélange de ces derniers.

25. Procédé conforme à la revendication 22, dans lequel, dans l'étape (B), le composé organique dihydroxylé est du bisphénol A et l'halogénure de carbonyle est du phosgène.

26. Procédé conforme à la revendication 22, dans lequel les étapes (A) et (B) sont toutes les deux effectuées dans un système biphasique comprenant une phase aqueuse et un solvant organique non-miscible à l'eau.

27. Procédé conforme à la revendication 22, dans lequel, dans l'étape (B), on maintient le pH à une valeur de 5 à 9 pendant la première partie de la réaction, et on l'augmente à une valeur de 10 à 13 pendant la dernière partie de la réaction.

28. Copolyestercarbonate séquencé conforme à la revendication 1, dans lequel le degré de polymérisation des séquences d'arylate vaut au moins 10.

29. Copolyestercarbonate séquencé conforme à la revendication 1, dans lequel le degré de polymérisation des séquences d'arylate vaut au moins 20.

30. Copolyestercarbonate séquencé conforme à la revendication 1, dans lequel le degré de polymérisation des séquences d'arylate vaut de 30 à 50.

31. Copolyestercarbonate séquencé conforme à la revendication 1, dans lequel le degré de polymérisation des séquences de carbonate vaut au moins 20.

32. Copolyestercarbonate séquencé conforme à la revendication 1, dans lequel le degré de polymérisation des séquences de carbonate vaut de 50 à 200.